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REPORT NO. 0235-01-19 (QUARTERLY)
PERIOD COVERED: 1 JANUARY-31 MARCH 1964

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2855(00)
ARPA ORDER NO. 170, AMENDMENT NO. 8
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APRIL 1964

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CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

(0235)

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April 1964

Report No. 0235-01-19
(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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A Report To

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract Nonr 2655(00)
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Project Code 4910

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Report No. 0235-01-19

ABSTRACT

1-Bromo-1,1-bis(difluoramino)butane was prepared by the reaction of 1,1-dibromo-1-nitrobutane with difluoramine in the presence of fuming sulfuric acid. 1-Bromo-1,1-dinitrobutane did not react under these conditions. Both 1-chloro-1-nitrosocyclohexane and 1-nitro-1-nitrosocyclohexane were converted rapidly to 1,1-bis(difluoramino)cyclohexane, indicating that the nitroso group is a useful leaving group for difluoramine reactions. N-Methyl-N-isopropylidene-N-fluoroammonium fluoborate was prepared from t-butyldifluoramine and boron trifluoride.

The fluorination of aqueous ureas was investigated in more detail. N-Fluoro-N-n-propylurea, unidentified in earlier work, was produced in the fluorination of n-propylurea together with n-propyldifluoramine and N,N-difluoro-N'-n-propylurea. The fluorination of aqueous urea led to the isolation of monofluorourea. The compound was fully characterized, and its reactions with acids and carbonyl compounds are described. Attempts to utilize fluorourea as an intermediate in the preparation of fluoramine have so far been unsuccessful.

2-Difluoraminoethylcarbonyl fluoride was prepared by fluorination of 2-imidazolidone in aqueous solution. The N-fluoro derivative was produced in the fluorination of methyl 2,2-dinitro-2-fluoroethylcarbamate.

Pure fluoroammonium perchlorate was obtained by means of vacuum sublimation of crude product derived from the reaction of isopropyl N-fluorocarbamate and 70% perchloric acid.

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Report No. 0235-01-19

CONTRACT FULFILLMENT STATEMENT

This is the nineteenth in a series of quarterly technical summary reports submitted in partial fulfillment of the contract. It covers the period 1 January through 31 March 1964.

AEROJET-GENERAL CORPORATION



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I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military applications.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

1,1-Dichloro-1-difluoraminoethane and 1-chloro-1,1-bis(di-fluoramino)ethane have been prepared by the reaction of difluoramine with vinylidene chloride in the presence of fuming sulfuric acid, as previously reported.* Under these conditions, 1,1-dichloro-1-nitrobutane was converted to 1,1-dichloro-1-difluoraminobutane.** During the current period, this study has been extended to other potential leaving groups, with the objective of finding a general method for preparing 1,1,1-tris(difluoramino)alkanes.

1,1-Dibromo-1-nitrobutane was synthesized by the reaction of 1-nitrobutane with an excess of aqueous sodium hypobromite. The reaction of this compound with refluxing difluoramine in fuming sulfuric acid for 4 hours gave a product that appeared to be a mixture of 1,1-dibromo-1-difluoraminobutane and 1-bromo-1,1-bis(difluoramino)butane, on the basis of elemental analysis. 1-Bromo-1,1-bis(difluoramino)butane was isolated, however, when this reaction was carried out for 2 hours at the reflux temperature of difluoramine, followed by 2 hours at ambient temperature under autogenous pressure. This compound was identified by elemental analysis, its infrared spectrum (Figure 1), and its proton and fluorine nuclear-magnetic-resonance (NMR) spectra (Figures 2 and 3, respectively). The fluorine NMR spectrum has the form of a nonequivalence

* Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 2730 (Summary), October 1963, p. 4 (Confidential).

** Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 0235-01-18 (Quarterly), January 1964, p. 1 (Confidential).

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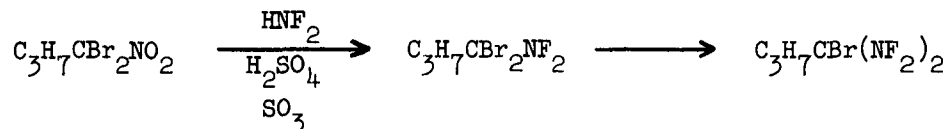
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quartet, which would be expected on the basis of geometric similarities to 1,1-bis(difluoramino)alkanes, which give this type of spectrum.*

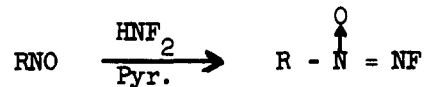
The same product was obtained when the reaction time was extended to 24 hours at ambient temperature:



Additional attempts will be made to replace the remaining bromine.

1-Bromo-1,1-dinitrobutane was synthesized in order to assess the reactivity of this general class of compounds. When it was treated with difluoramine in fuming sulfuric acid for 20 hours at ambient temperature, however, only unreacted starting material was recovered.

Nitroso compounds have been reported to react with difluoramine and pyridine to form N-fluoroazoxy compounds:**



No work has been reported on the use of nitroso groups as leaving groups for acid-catalyzed difluoramine reactions.

When 1-chloro-1-nitrosocyclohexane*** was added to refluxing difluoramine in fuming sulfuric acid, the blue color of the starting material disappeared instantaneously, and a gas was evolved. Workup after 2 hours yielded only 1,1-bis(difluoramino)cyclohexane,**** identified by its infrared spectrum:

* Rohm & Haas Company Quarterly Progress Report on Synthetic Chemistry, Part II, 18 August 1961, p. 18 (Confidential).

** Rohm & Haas Company Quarterly Progress Report on ARPA Projects, No. P-61-21, 25 October 1961, p. 1 (Confidential).

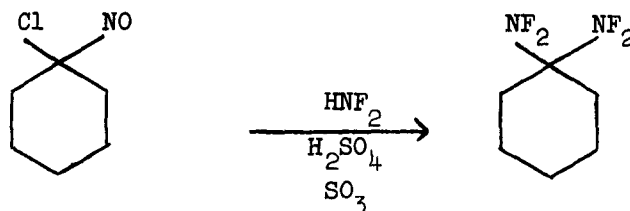
*** E. Müller, H. Metzger, and D. Fries, Ber., 87, 1454 (1954).

**** Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 0235-01-10 (Quarterly), 14 April 1961, Figure 3 (Confidential).

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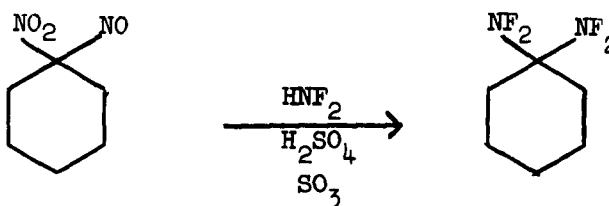
II Technical Discussion, A (cont.)

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The nitroso group may be removed by direct protonation, followed by loss of HNO , or possibly through the formation of a fluoroazoxy intermediate that undergoes protonation and cleavage.

Under the same experimental conditions, 1-nitro-1-nitrosocyclohexane^{*} was treated with difluoramine. The only product that was isolated after a 2-hour reaction period was 1,1-bis(difluoramino)cyclohexane. A possible intermediate in this reaction is the 1,1-nitrodifluoramino. In the hope of isolating an intermediate, the reaction was repeated but was quenched with ice 5 min after addition of the starting material was completed. Again, the only product isolated was 1,1-bis(difluoramino)cyclohexane:



This reaction will be repeated using less-acidic catalysts.

The reaction of 1-methyl-1-difluoraminocyclohexane with boron trifluoride has been shown to yield an immonium fluoborate as follows:^{**}

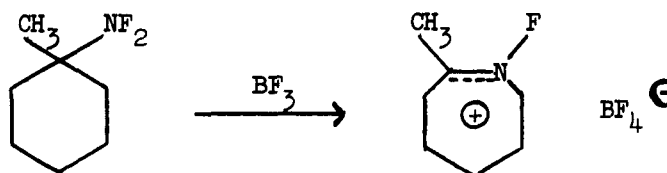
^{*} Nemetkin, Chem. Zentr., 1910 II, 1377.

^{**} Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 0235-01-16 (Quarterly), March 1963, pp. 4-5 (Confidential).

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The analogous salt derived from t-butyldifluoramine has now been prepared and identified by elemental analysis. The reaction was conducted by bubbling boron trifluoride through a pentane solution of t-butyldifluoramine at -80°C , and resulted in a 59.5% yield of N-methyl-N-isopropylidene-N-fluoroammonium fluoborate. The starting material, t-butyldifluoramine, was prepared in 63% yield from isobutylene and difluoramine in the presence of the boron trifluoride complex of phosphoric acid.

2. Experimental

a. 1,1-Dibromo-1-nitrobutane

Bromine (35 ml, 102.4 g, 0.642 mole) was added dropwise to a solution of 103 g (2.56 moles) of sodium hydroxide in 1.03 liters of water, maintained at 0 to 5°C . 1-Nitrobutane (30 g, 0.292 mole) was then added dropwise and the mixture was kept at $0-5^{\circ}\text{C}$, with stirring, for 2 hours and 20 min. A heavy liquid precipitated. This liquid was separated, and the aqueous layer was extracted with 50 ml of methylene chloride. The combined organic layers were dried over sodium sulfate, and the solvent was distilled off. The residue was vacuum-distilled to give 1 g of liquid, b.p. $< 45^{\circ}\text{C}/3$ mm Hg, and 72.8 g (0.279 mole, 95.5% yield) of 1,1-dibromo-1-nitrobutane, n_D^{25} 1.5035.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{NO}_2\text{Br}_2$: C, 18.4; H, 2.78; N, 5.37.

Found: C, 18.5; H, 2.72; N, 5.42.

b. Reaction of 1,1-Dibromo-1-nitrobutane with Difluoramine

1,1-Dibromo-1-nitrobutane (4.0 g, 0.0153 mole) was added dropwise to a stirred mixture of 11 ml of 20% fuming sulfuric acid and 27 g of difluoramine in a reactor fitted with Fischer-Porter glass needle valves. The

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mixture was allowed to reflux for 2 hours. The valves were then closed and the reaction was allowed to proceed at ambient temperature for an additional 2 hours. The color of bromine in the solution became pronounced during this period.

The reactor was cooled to -80°C , and 50 ml of pentane was added. The reaction mixture was allowed to warm to room temperature, with stirring, to remove unreacted difluoramine. The sulfuric acid layer was added to 100 ml of ice and was extracted with three 30-ml portions of methylene chloride. Distillation of the methylene chloride gave no residue.

The pentane layer was dried over sodium sulfate and was distilled to yield 0.47 g of a slightly yellow liquid, b.p. $36^{\circ}\text{C}/15\text{ mm}$.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{N}_2\text{F}_4\text{Br}$: C, 20.1; H, 2.93; N, 11.70; F, 31.8.

Found: C, 21.1; H, 3.14; N, 11.4; F, 28.6.

The proton NMR spectrum (Figure 2) was taken with carbon tetrachloride as the solvent and tetramethylsilane (TMS) as the internal reference. The irregular triplet at 0.99 ppm is assigned to the terminal methyl group. The multiplet with maximum intensity at 108 cps corresponds roughly to the sextet expected for the $-\text{CH}_2\text{CH}_2\text{CH}_3$ methylene. The fluorine NMR spectrum (CCl_4 solution, CFCl_3 internal reference) consists of a "nonequivalence quartet," with chemical shifts of -35.11 and -46.27 ppm and a coupling constant of 604 cps.

c. 1,1-Dinitro-1-bromobutane

Bromine (17.0 g, 0.0106 mole) was added dropwise, with stirring, at ambient temperature to a solution of 4.0 g (0.10 mole) of sodium hydroxide and 15.00 g (0.10 mole) of 1,1-dinitrobutane in 100 ml of water. A heavy oil precipitated; it was separated, added to 25 ml of methylene chloride, dried over sodium sulfate, and distilled, to yield 17.4 g (0.077 mole, 77% yield) of 1,1-dinitro-1-bromobutane, b.p. $43^{\circ}\text{C}/0.65\text{ mm}$, n_D^{25} 1.4673.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{N}_2\text{O}_4\text{Br}$: C, 21.15; H, 3.08; N, 12.33.

Found: C, 22.1; H, 3.34; N, 11.8.

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II Technical Discussion, A (cont.)

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d. Reaction of 1,1-Dinitro-1-bromobutane with Difluoramine

1,1-Dinitro-1-bromobutane (4.0 g) was added to a refluxing mixture of 11 ml of 20% fuming sulfuric acid and approximately 27 g of difluoramine in a reactor fitted with Fischer-Porter glass needle valves. The mixture was allowed to reflux, with stirring, at atmospheric pressure for 2 hours. The valves were closed and the reaction mixture was allowed to stand at ambient temperature under autogenous pressure for 20 hours. Unreacted difluoramine was removed, and the material remaining was added dropwise to 100 ml of crushed ice. This mixture was extracted with two 50-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and was distilled to give 3.37 g (84% recovery) of 1,1-dinitro-1-bromobutane, b.p. $43^{\circ}\text{C}/0.68\text{ mm}$.

e. Reaction of 1-Chloro-1-nitrosocyclohexane with Difluoramine

1-Chloro-1-nitrosocyclohexane* (5.0 g, 0.0399 mole) was added dropwise, with stirring, to a refluxing mixture of 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. The blue color of the nitroso compound disappeared instantaneously, and a gas was evolved. After 2 hours, the excess difluoramine was removed and the reaction mixture was quenched with 100 ml of ice. The product was extracted with three 30-ml portions of methylene chloride, and the methylene chloride solution was dried over sodium sulfate and distilled through a 25-cm platinum spiral column. Vacuum distillation of the residue gave 2.06 g (0.0105 mole, 31% yield) of 1,1-bis(difluoramino)cyclohexane, identified by its infrared spectrum.

f. Reaction of 1-Nitro-1-nitrosocyclohexane with Difluoramine

A solution of 5.0 g (0.0316 mole) of 1-nitro-1-nitrosocyclohexane in 15 ml of methylene chloride was added dropwise to a stirred mixture of 27 g of difluoramine and 11 ml of 20% fuming sulfuric acid. The blue nitroso color disappeared immediately. The reaction mixture was drained

*Müller, et al., op. cit.

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onto 200 ml of ice 5 min after the addition was completed, and the product was extracted with 75 ml of methylene chloride. The methylene chloride solution was dried over sodium sulfate and was distilled through a 25-cm platinum spiral column to yield 1.92 g (0.0098 mole, 31% yield) of 1,1-bis(difluoramino)cyclohexane, b.p. 35°C/5 mm, identified by its infrared spectrum.*

g. t-Butyldifluoramine

Isobutylene (22 ml, 13 g, 0.232 mole) was added to 27 g of refluxing difluoramine, and 1 ml of the boron trifluoride complex of phosphoric acid was added. An additional 1 ml of this catalyst was added after 1 hour and the mixture was allowed to reflux for 3 hours. n-Decane (100 ml) was then added and the unreacted difluoramine was removed. Distillation of the decane solution gave 15.9 g (0.146 mole, 63% yield) of t-butyldifluoramine, b.p. 40°C.

h. N-Methyl-N-isopropylidene-N-fluoroammonium Fluoborate

A solution of 3.0 g (0.0275 mole) of t-butyldifluoramine in 15 ml of pentane was placed in a three-necked 50-ml flask fitted with gas inlets for nitrogen and boron trifluoride, a drying tube, and a magnetic stirrer. The flask was immersed in a -80°C bath, and nitrogen and boron trifluoride were bubbled through the solution until no further reaction was evident. A white solid precipitated. This solid was filtered in a dry box under nitrogen and was dried under vacuum to give 2.9 g (0.0164 mole, 59.5% yield) of N-methyl-N-isopropylidene-N-fluoroammonium fluoborate, m.p. 134-138°C (d).

Anal. Calcd. for $C_{14}H_{29}NF_5B$: C, 27.1; H, 5.08; N, 7.91; F, 53.6.

Found: C, 26.9; H, 5.22; N, 7.80; F, 51.9.

B. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

a. Fluorination of Monoalkylureas

The fluorination of aqueous monoalkylureas has been reported** to give the corresponding alkyl difluoramines and N,N-difluoro-N'-alkylureas:

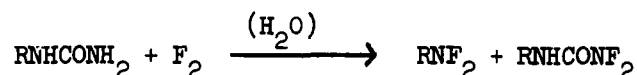
* Aerojet-General Report 0235-01-10, loc. cit.

** Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 2099 (Annual Summary), 7 November 1961, p. 17 ff. (Confidential).

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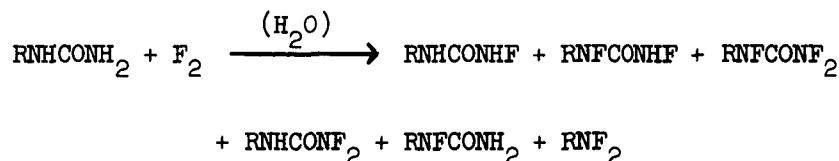
II Technical Discussion, B (cont.)

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The fluorination of aqueous n-propylurea was recently repeated on a larger scale and a new NF compound was isolated, in addition to the N,N-difluoro-N'-n-propylurea and n-propyldifluorammine found previously. This new compound was identified as N-fluoro-N-n-propylurea, $\text{C}_3\text{H}_7\text{NFCONH}_2$, by its elemental analysis, its NMR spectra (Figures 4 and 5), and its infrared spectrum (Figure 6). n-Propyldifluorammine and N,N-difluoro-N'-n-propylurea were characterized by their elemental analyses and their infrared spectra.

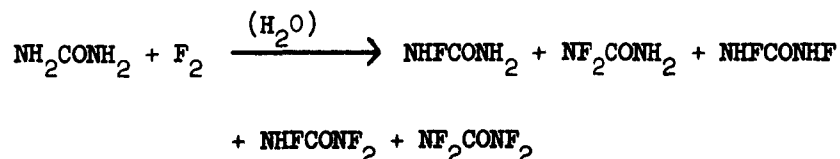
The fact that N-alkyl-N-fluoroureas were overlooked in the early work, mainly because of small-scale experiments, suggested the possibility that other NF compounds may have been missed also. Theoretically, six compounds should be formed in the fluorination of monoalkylureas, but only three (the last three in the series below) have been isolated and identified:



Attempts are being made to determine whether the other three possible NF compounds can be prepared.

b. Monofluorourea

The isolation of a new NF compound in the alkylurea series indicated that the fluorination of urea itself should be examined in more detail. This reaction, now utilized to synthesize N,N-difluorourea (the intermediate for the preparation of difluorammine), should theoretically produce four additional compounds:



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II Technical Discussion, B (cont.)

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It is possible that some of the other expected fluoroureas, if formed at all, are unstable under the reaction conditions. On the other hand, it is also possible that some, or even all, of these compounds could be synthesized and isolated by varying the reaction conditions and by improving the workup techniques. In conjunction with the fact that all of the possible chlorine derivatives of urea have been reported,* these considerations emphasized the need for further study.

The study was initiated with an effort to synthesize monofluorourea using a 1-to-1 molar ratio of fluorine to urea. The fluorine NMR spectrum of the aqueous fluorination mixture was compared with that of urea fluorinated at a 2-to-1 molar ratio of fluorine to urea. One additional resonance peak signified the presence of a new NF compound, possibly monofluorourea. Initial attempts to isolate this new compound failed, due to high solubility in water and low concentration in the fluorination mixture. The concentration of urea was increased from 8-10% to 30-40%. The fluorination proceeded smoothly at the higher concentration and batches containing 4 moles of urea were easily fluorinated in 1 to 1.5 hours. The resulting solution was partially neutralized with sodium bicarbonate to avoid excessive etching of the glass equipment, and a mixture of the new compound and N,N-difluorourea was extracted with diethyl ether. The mixture was separated by recrystallization from methylene chloride, in which the new compound was sparingly soluble. The crystalline solid was identified as monofluorourea on the basis of its elemental analysis, its infrared spectrum (Figure 7), and its proton and fluorine NMR spectra (Figures 8 and 9, respectively). The fluorine NMR spectrum of fluorourea in several solvents (water, tetrahydrofuran, diethyl ether) was obtained; in all cases, a single absorption peak was observed, as opposed to the expected doublet. A plausible explanation for this anomaly is to assume that the hydrogen of the HNF group of fluorourea undergoes a rapid, acid-catalyzed exchange involving the solvent. The chemical reactions of fluorourea establish its structure beyond any doubt; hence, nothing more will be done to resolve this variance.

*German Patent 720,206 (1935).

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II Technical Discussion, B (cont.)

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Fluorourea is a white, nonhygroscopic solid, m.p. 56-57°C. The compound has been stored at 0°C for several months without noticeable decomposition. When stored at room temperature, fluorourea gradually turns yellow; the resulting yellow solid was identified as azodicarbonyldiamide, $\text{NH}_2\text{CON}=\text{NCONH}_2$. Aqueous solutions of fluorourea can also be stored for several weeks at 0°C; at room temperature, however, azodicarbonyldiamide gradually deposits. Aqueous fluorourea in the presence of urea at room temperature results in the formation of biurea instead of azodicarbonyldiamide. Fluorourea is very soluble in ethers, alcohols, and concentrated acids but is only sparingly soluble in alkanes and halocarbons.

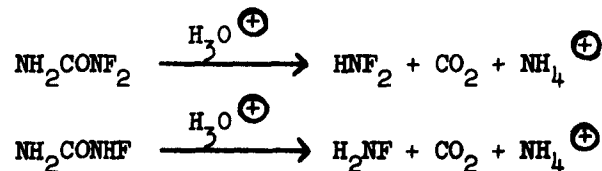
The impact sensitivity of fluorourea was determined with a Bureau of Mines type of tester and a 2-kg weight. With this machine, RDX on the bare anvil exhibits 50% firings at a 30-cm drop distance. The following values, in 2-kg-weight drop distance for 50% firings, were obtained for monofluorourea:

<u>Surface</u>	<u>Drop Distance, cm</u>
Bare anvil	34
Grit paper	30
Glass-fiber cloth	17

Differential thermal analysis shows that fluorourea exhibits an exotherm at 128°C.

The fluorourea needed for further study was made in batches up to 45 g in size and 20% in yield. No attempts were made to maximize the yield; N,N-difluorourea was obtained as a byproduct in all preparations.

It was thought that fluorourea might be useful as a starting material for the preparation of fluoramine, just as N,N-difluorourea is used to generate difluoramine:



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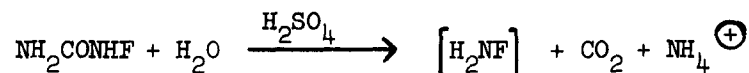
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II Technical Discussion, B (cont.)

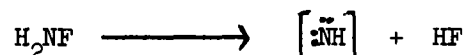
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Numerous reactions of fluorourea have been investigated, but so far all attempts to generate fluoramine have failed. The investigations are discussed below.

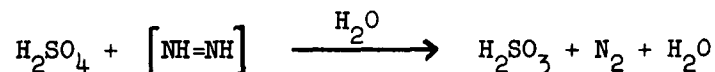
A solution of fluorourea in 50% sulfuric acid was warmed to 60°C, simulating conditions used in generating difluoramine from difluorourea. The reaction was complete in 1 hour, as evidenced by carbon dioxide evolution, but no NF compound was evolved. On dilution of the reaction mixture with ethanol, ammonium sulfite precipitated. It appears that fluorourea underwent hydrolysis as anticipated:



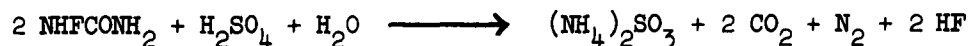
Fluoramine apparently decomposed under these conditions:



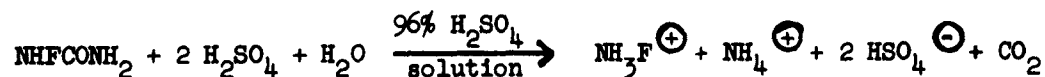
and the resulting imine (or diimine) reduced sulfuric acid to sulfite:



In summary, the overall reaction in 50% aqueous sulfuric acid can be represented as follows:



A dilute solution of fluorourea in 96% concentrated sulfuric acid was warmed to 40-50°C. Carbon dioxide was liberated at a rapid rate, and the reaction was complete in 15 min. The sulfuric acid solution contained N-fluoroammonium cation, as shown by its fluorine NMR spectrum. Upon dilution with tetrahydrofuran, an equimolar mixture of fluoroammonium bisulfate and ammonium bisulfate was obtained in the form of a white crystalline solid, in accordance with the following reaction:



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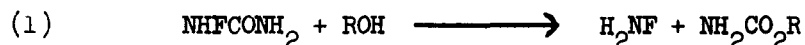
II Technical Discussion, B (cont.)

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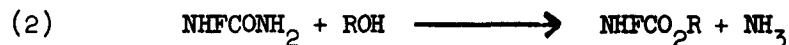
Using only enough 96% sulfuric acid to conform with the stoichiometry of the above reaction,* some carbon dioxide but no NF compound was evolved, and the reaction mixture solidified after 30 min at 30-35°C. The major products were hydrazine sulfate and ammonium sulfate. The change in the course of the reaction appears to be due to lack of sufficient water for hydrolysis to occur.

Finally, fluorourea was hydrolyzed in 93% sulfuric acid using a 2.5-to-1 molar ratio of sulfuric acid to fluorourea and a 1-to-1 molar ratio of water to fluorourea. A white solid identified as an equimolar mixture of fluoroammonium bisulfate and ammonium bisulfate precipitated upon dilution of the reaction mixture with tetrahydrofuran.

Alcoholysis of fluorourea was studied as another approach to the preparation of fluoramine. It was hoped that the reaction would follow the first of the two potential courses indicated below.



or



A solution of fluorourea in ethanol was refluxed for several hours. A small amount of azodicarbonydiamide, $\text{NH}_2\text{CON}=\text{NCONH}_2$, was produced instead of the expected products, and most of the fluorourea was recovered unchanged. Turning to a higher-boiling alcohol and more vigorous reaction conditions, biurea was obtained when a solution of fluorourea in ethylene glycol was heated. Apparently, some of the fluorourea oxidized glycol and in turn was reduced to urea; this urea then coupled with fluorourea, producing biurea.

* Actual amounts of reagents used were 4.0 g of 96% sulfuric acid (~ 0.04 mole) and 1.6 g (0.02 mole) of fluorourea. This amount of sulfuric acid contains only 0.16 g (0.009 mole) of water, insufficient for the following reaction:



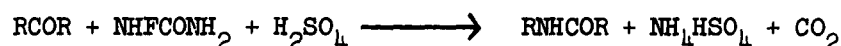
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II Technical Discussion, B (cont.)

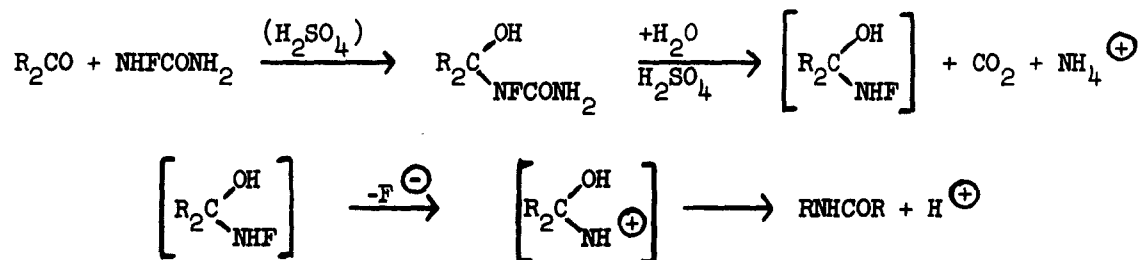
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Fluorourea dissolved in acetic anhydride at room temperature without apparent reaction. Cyanuric acid was formed when this solution was heated to 65-70°C.

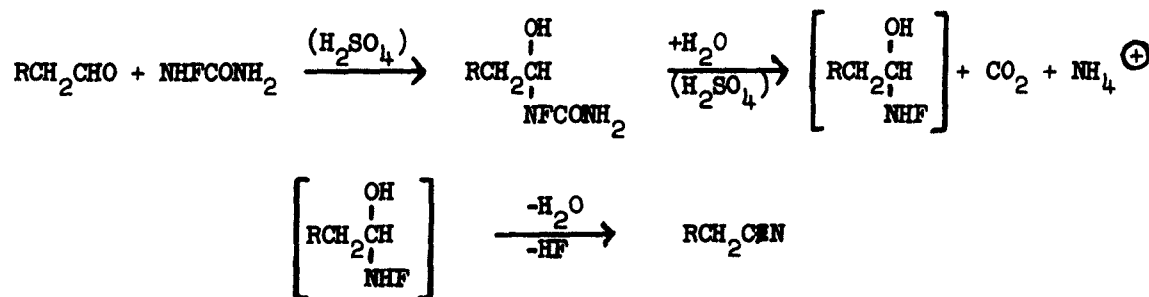
In the presence of concentrated sulfuric acid, fluorourea reacts with aldehydes and ketones, producing nitriles and amides, respectively:



The reaction is rapid and complete; a solution of fluorourea in 3-pentanone was "titrated" with concentrated sulfuric acid until the evolution of carbon dioxide ceased. After removal of ammonium bisulfate and excess ketone, N-ethylpropionamide was obtained in almost quantitative yield. Since fluorourea reacts slowly with concentrated sulfuric acid at room temperature, and does not react at all with ketones in the absence of an acid, it seems that reaction with ketones involves the formation of a 1-to-1 adduct, which in turn undergoes hydrolysis and rearrangement as shown below.



A similar consideration applies to the reaction of fluorourea with aldehydes:



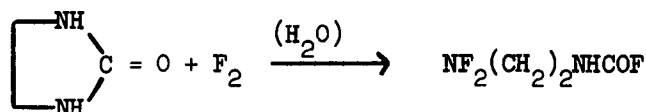
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II Technical Discussion, B (cont.)

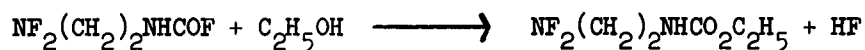
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c. Fluorination of Cyclic Ureas

The fluorination of aqueous 2-imidazolidone followed a course similar to that observed with tetrahydro-2-pyrimidone* previously. The major product of the reaction was identified as 2-difluoraminoethylcarbamy fluoride on the basis of elemental analysis, infrared spectrum (Figure 10), and NMR spectra (Figures 11 and 12):



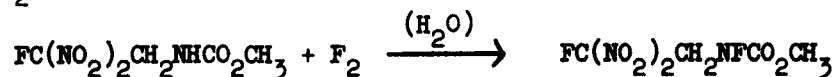
Some of the material was converted to the corresponding carbamate by reaction with ethanol:



The forerun material obtained in the distillation of 2-difluoraminoethylcarbamy fluoride exhibited a typical isocyanate absorption peak in the infrared, suggesting the presence of small amounts of 2-difluoraminoethylisocyanate. In the fluorination of tetrahydro-2-pyrimidone, the corresponding isocyanate was produced in higher yields and was completely characterized.

d. Fluorination of Carbamates

The fluorination of methyl 2,2-dinitro-2-fluoroethyl-carbamate** produced only methyl N-fluoro-N-(2,2-dinitro-2-fluoroethyl)carbamate, as shown below, and none of the desired 2,2-dinitro-2-fluoroethyldifluoramine, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{NF}_2$.



The compound was characterized by elemental analysis, infrared spectrum (Figure 13), and NMR spectra (Figures 14 and 15).

*Aerojet-General Report 0235-01-18, p. 8.

**Ibid., p. 18, for preparation.

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II Technical Discussion, B (cont.)

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2. Experimental

a. Fluorination of n-Propylurea

A solution of 102 g (1.0 mole) of n-propylurea in 700 ml of water was fluorinated at 0-5°C until 1.5 moles of fluorine was consumed (6 hours). The reaction flask was connected in series with a -80°C trap to condense volatile reaction products. At the end of the run, 15 g of a colorless liquid, identified as n-propyldifluoramine, was present in the trap. The crude material was purified by distillation, b.p. 45°C, 99% pure as determined by gas chromatography.

Anal. Calcd. for $C_3H_7NF_2$: C, 37.9; H, 7.4; N, 14.7; F, 39.95.

Found: C, 37.8; H, 7.4; N, 14.7; F, 40.0.

The infrared spectrum of the material was in agreement with the difluoramine structure.

The aqueous-fluorination mixture was extracted with three 50-ml portions of methylene chloride, followed by five 50-ml portions of diethyl ether. All extracts were combined, dried, and filtered. The filtrate was concentrated to remove solvents, and the pale-yellow residual liquid (30 g) was fractionated to give 9.1 g of a colorless liquid, b.p. 40-50°C/0.1 mm, and 4.0 g of a liquid, b.p. 60-70°C/0.2 mm, that solidified in the receiver.

The liquid product was redistilled to give 8.0 g of material, b.p. 40°C/0.1 mm, n_D^{25} 1.4045, that was identified as N,N-difluoro-N'-n-propylurea.

Anal. Calcd. for $C_4H_8NF_2O$: C, 34.8; H, 5.8; N, 20.3; F, 27.5.

Found: C, 34.6; H, 5.9; N, 20.1; F, 27.8.

Its infrared spectrum was similar to that of N,N-difluoro-N'-ethylurea.*

The 60-mc proton NMR spectrum was obtained using a carbon tetrachloride solution with TMS added as an internal reference. The assignments are as follows: The triplet at 0.99 ppm is assigned to the propyl methyl group,

*Aerojet-General Report 0235-01-10, Figure 13.

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II Technical Discussion, B (cont.)

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$\text{CH}_3\text{CH}_2\text{CH}_2-$. The sextet at 1.65 ppm is assigned to the internal methylene, $\text{CH}_3\text{CH}_2\text{CH}_2-$. The slightly broadened quartet at 3.29 ppm is assigned to the methylene adjacent to the nitrogen, $-\text{CH}_2\text{NH}-$. The broadened signal at 7.07 ppm is assigned to the amide proton.

The 56.4-mc fluorine NMR spectrum was obtained using the same sample, with Freon-11 added as an internal reference. The spectrum consists of a single, somewhat broadened signal of -1841 cps (-32.64 ppm) assigned to the difluoramino group.

The solid product was purified by crystallization from carbon tetrachloride to give 1.5 g of a white crystalline solid, m.p. 78°C, that was identified as N-fluoro-N-n-propylurea.

Anal. Calcd. for $\text{C}_4\text{H}_9\text{N}_2\text{FO}$: C, 40.0; H, 7.6; N, 23.3; F, 15.8.

Found: C, 39.9; H, 7.6; N, 23.1; F, 16.0.

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained using TMS and Freon-11 as internal references and CDCl_3 as the solvent. The fluorine spectrum (Figure 5) consists of a triplet at +66.7 ppm (splitting 39.7 cps). The proton NMR spectrum (Figure 4) consists of a triplet at 0.99 ppm, a sextet centered at 1.74 ppm, a pair of triplets centered at 3.66 ppm, and a broad signal at 6.04 ppm. The triplet at 0.99 ppm is assigned to the CH_3CH_2- protons. The sextet is assigned to the $\text{CH}_3\text{CH}_2\text{CH}_2-$ protons. The spacing between the pair of triplets (39.2 cps) compares favorably with the triplet splitting (39.7 cps) observed in the fluorine spectrum and is assigned to the $-\text{CH}_2\text{CH}_2\text{NF}-$ protons. The broad signal at 6.04 ppm is assigned to the $-\text{NFCONH}_2$ protons.

The proton and fluorine NMR spectra are consistent with each other and with the structure indicated above.

The infrared spectrum of N-fluoro-N-n-propylurea is shown in Figure 6.

The distillation residue, amounting to 11 g, was accidentally lost after removal of the two compounds above.

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II Technical Discussion, B (cont.)

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b. Fluorourea

(1) Preparation and Analysis

A solution of 120 g (2.0 moles) of urea in 300 ml of water was fluorinated at 0-5°C until 2.0 moles of fluorine was consumed. The fluorination time was 1.5 hours. The reaction mixture was extracted with seven 150-ml portions of diethyl ether; the combined ethereal extracts were dried and treated with 100 g of sodium fluoride to complex the dissolved hydrogen fluoride. The ethereal solution was concentrated to remove the solvent, and the residual viscous liquid* was dissolved in 2.0 liters of boiling methylene chloride. After the methylene chloride solution was cooled (first to 25°C and then to 0-5°C), fluorourea crystallized in the form of large plates, m.p. 56-57°C, yield 32 g (20%).

Anal. Calcd. for $\text{CH}_2\text{N}_2\text{FO}$: C, 15.39; H, 3.88; N, 35.89; F, 24.34.

Found: C, 15.3; H, 4.2; N, 35.8; F, 23.7.

In another experiment, a solution of 240 g (4.0 moles) of urea in 350 ml of water was fluorinated in the same manner as before. At the end of the fluorination, the aqueous reaction mixture was partially neutralized by portionwise addition of 188 g (2.0 moles) of solid sodium bicarbonate at 0-5°C, with stirring, over a period of 30 min. The solution was filtered to remove sodium fluoride. Fluorourea was isolated from the filtrate in 20% yield.

The infrared spectrum of fluorourea (NaCl wafer) is shown in Figure 7.

The 56.4-mc fluorine NMR spectrum was obtained in aqueous solution, using trifluoroacetic acid as an external reference. The spectrum consisted of two signals, at +31.88 ppm and +50.65 ppm. The signal at +50.65 ppm is assigned to hydrofluoric acid. (Aqueous hydrofluoric acid in

* This residue is a mixture of N,N-difluorourea and fluorourea. N,N-Difluorourea is very impact-sensitive and toxic; therefore, all precautions should be taken to shield the operator from a possible explosion.

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II Technical Discussion, B (cont.)

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a Pyrex tube exhibits two major peaks at about +51.2 and +71.4 ppm.) The signal at +31.88 ppm was tentatively assigned to the fluorine of NHFCO- . The lack of splitting in the fluorine resonance might be due to proton exchange. This postulate is partially substantiated by the fact that the fluorine NMR spectrum of methyl N-fluorocarbamate in water solution also consists of a single sharp peak at +41.34 ppm with trifluoroacetic acid (TFA) used as an external reference, indicating proton exchange between NHF- and water.

In order to reduce the proton exchange, the fluorine NMR spectrum of fluorourea was again obtained, with diethyl ether and tetrahydrofuran (Figure 9) used as solvents. Single peaks were observed in both solvents. The signal was measured in diethyl ether at +34.33 ppm, and in tetrahydrofuran at +34.22 ppm, both with reference to TFA as an external standard.

The proton NMR spectrum (Figure 8) was obtained in tetrahydrofuran, using TMS as an internal reference. The spectrum was compared with that of tetrahydrofuran. It contains two additional signals (6.67 and 10.66 ppm); both are broadened and their area: appear to approach a 2-to-1 ratio.

(2) Reactions

(a) With 50% Sulfuric Acid

A solution of 2.0 g (0.0026 mole) of fluorourea in 20 ml of 50% sulfuric acid (by volume) was warmed, with stirring, to 65°C and was left at this temperature until the evolution of gas ceased (1 hour). The resulting solution was cooled to 25°C and was diluted with 50 ml of ethanol, resulting in the deposition of a white solid. The solid was filtered and washed with ethanol, followed by diethyl ether. The solid amounted to 1.7 g, m.p. 255-258°C. A sample of the material was recrystallized from water-ethanol mixture, m.p. 265-270°C. Its infrared spectrum, melting point, and "mixed" melting point were identical with those of an authentic sample of ammonium sulfite.

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(b) With Large Excess of Concentrated Sulfuric Acid

A solution of 0.3 g of fluorourea in 3.0 g of 96% sulfuric acid was warmed to 40-50°C; vigorous gas evolution occurred. The reaction was completed in 5 to 10 min. The 56.4-mc fluorine NMR spectrum of the resulting solution (TFA as an internal reference) consisted of a quartet (splitting 43.6 cps) centered at 35.24 ppm with a 1:3:3:1 ratio of component intensities, indicating the presence of the $\text{NH}_3\text{F}^{\oplus}$ structure.*

(c) With Stoichiometric Amount of Concentrated Sulfuric Acid

A solution of 1.6 g (0.02 mole) of fluorourea in 4.0 g (~0.04 mole) of 96% sulfuric acid was warmed to 35°C, resulting in gas evolution. After 30 min the reaction mixture began to foam vigorously and then solidified; it was allowed to cool to 25°C and was treated with 35 ml of absolute ethanol. The ethanol-insoluble solid (1.0 g) was removed by filtration and recrystallized from hot water, m.p. 245°C (d), alone or when mixed with an authentic sample of hydrazine sulfate. Its infrared spectrum was identical with that of hydrazine sulfate.

After removal of hydrazine sulfate, the ethanolic solution was diluted with 50 ml of diethyl ether, resulting in precipitation of a white solid. The material was recrystallized from a water-ethanol mixture to give 1.0 g of a crystalline solid, m.p. 265-275°C, alone or when mixed with an authentic sample of ammonium sulfite.

(d) Hydrolysis with Concentrated Sulfuric Acid

A solution of 1.6 g (0.02 mole) of fluorourea in 6.0 g of 93% sulfuric acid was allowed to stand at room temperature for 72 hours. A slow gassing continued for a period of 24 hours, and the gaseous material was identified as carbon dioxide (infrared spectrum). The reaction mixture was added, with stirring, to 100 ml of tetrahydrofuran, and a white solid precipitated. The solid was filtered and the filter cake was washed several times with

*Research in Fluoro-Nitro Compounds (U), Aerojet-General Report 2381 (Annual Summary), 15 October 1962, p. 32 (Confidential).

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tetrahydrofuran in a dry nitrogen atmosphere. The vacuum-dried material amounted to 5.0 g.

Anal. Calcd. for 50/50% mixture of $\text{NH}_4^+ \text{HSO}_4^-$ and $\text{NH}_3\text{F}^+ \text{HSO}_4^-$: N, 11.4; F, 7.1.
Found: N, 12.1; F, 5.9.

(e) With Ethylene Glycol

A solution of 4.5 g of fluorourea in 25 ml of ethylene glycol was gradually heated to 140-145°C and was kept at that temperature for 30 min. Gas evolution started at 70-75°C, and the solution gradually deposited a white solid. The reaction mixture was cooled to 25°C; the solid product was removed by filtration and was recrystallized from water to give 1.2 g of material, m.p. 260-264°C, alone or when mixed with biurea. Its infrared spectrum was identical with that of biurea. An additional amount of biurea (0.7 g) was isolated from the ethylene glycol filtrate.

(f) With Acetic Anhydride

A solution of 4.7 g (0.06 mole) of fluorourea in 40 g of acetic anhydride was allowed to stand at 25°C for 24 hours. No visible reaction occurred. The solution was warmed to 75-80°C, resulting in vigorous gassing and gradual deposition of a white solid. The escaping gas was passed into concentrated sulfuric acid with the objective of converting fluoramine (if it was produced) to its fluoroammonium salt. No oxidizing species were detected in the sulfuric acid at the end of the run. At the end of 2 hours, the reaction mixture was cooled to 25°C; the solid was then filtered and was washed with diethyl ether. The crude material (1.3 g) was recrystallized from water, m.p. > 300°C, and was identified as cyanuric acid (infrared spectrum).

(g) With 3-Pentanone

Over a period of 10 to 15 min, 4.0 g (0.04 mole) of 96% sulfuric acid was added dropwise, with stirring, to a solution of 3.1 g (0.04 mole) of fluorourea in 8 ml of 3-pentanone. The reaction was exothermic and the reaction mixture was cooled externally to keep it below 50°C. The reaction mixture was filtered to remove ammonium bisulfate. The filtrate was deacidified with solid sodium bicarbonate, and was then filtered

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and concentrated to remove 3-pentanone. The residual liquid was distilled to give 4.0 g of N-ethylpropionamide, b.p. 55-56°C/0.1 mm (% N: calcd., 13.9; found, 13.7).

(h) With n-Butyraldehyde

Over a period of 10 min, 4.0 g (0.04 mole) of 96% sulfuric acid was added dropwise, with stirring, to a solution of 3.1 g (0.04 mole) of fluorourea and 2.8 g (0.04 mole) of n-butyraldehyde in 60 ml of diethyl ether. The reaction was exothermic and the ether refluxed. At the end of the run ammonium bisulfate was removed by filtration. The filtrate was deacidified with solid sodium bicarbonate and was filtered; this filtrate was then concentrated, and the residual liquid was distilled to give 2.0 g of n-butyronitrile (identified by infrared spectrum), slightly contaminated with n-butyraldehyde.

c. 2-Difluoraminoethylcarbonyl Fluoride

A solution of 43 g (0.5 mole) of 2-imidazolidone in 650 ml of water was fluorinated at 0-5°C until 22.5 liters of fluorine was consumed (2.0 hours). The clear and colorless reaction mixture was extracted with five 50-ml portions of methylene chloride. The combined extracts were dried, deacidified with 20 g of solid sodium bicarbonate, filtered, and concentrated. The residual liquid (18 g) was fractionated. After removal of a small forerun, the bulk of the liquid distilled at 39-40°C/0.05 mm, and was identified as 2-difluoraminoethylcarbonyl fluoride.

Anal. Calcd. for $C_3H_5N_2F_2O$: C, 25.3; H, 3.55; N, 19.7; F, 40.1.

Found: C, 25.4; H, 3.4; N, 19.5; F, 39.7.

The infrared spectrum of the compound is shown in Figure 10.

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained using a $CDCl_3$ solution with TMS and $CFCl_3$ as internal references. The spectra are consistent with each other and with the suggested structure. The assignments are discussed below.

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(1) Proton NMR Spectrum (Figure 11)

The broadened signal at 5.93 ppm is assigned to the amide proton. The remainder of the spectrum consists of irregular triplets centered at about 194 cps and 252 cps, and a complex multiplet with its maximum intensity at 220 cps. The 194- and 252-cps triplets are regarded as the outer members of a triplet of triplets assignable to the $\text{NF}_2\text{CH}_2\text{CH}_2$ - protons. The central member of the signal assignable to the $-\text{CH}_2\text{CH}_2\text{-NHCO-}$ protons overlap to form the 220-cps multiplet. On the basis of this assignment, the HF coupling constant is approximately 29 cps. The weak signal at 2.18 ppm is presumably due to an impurity.

(2) Fluorine NMR Spectrum (Figure 12)

The broadened triplet (splitting 27.5 cps) at -53.67 ppm is assigned to difluoramino fluorines, NF_2CH_2 -. The splitting observed is in satisfactory agreement with that obtained from the proton spectrum (29 cps) and is probably more accurate. The two doublets toward the high field, one relatively intense at +14.73 ppm (splitting 7.4 cps) and the other relatively weak at +20.74 ppm (splitting 20.2 cps), may be assigned to the different configurations (cis and trans) of the $-\text{NHCOF}$ fluorine. The splitting is attributed to coupling with the $-\text{NH-}$ proton.

d. Ethyl 2-Difluoraminoethylcarbamate

A solution of 3.0 g of 2-difluoraminoethylcarbamy fluoride in 50 ml of absolute ethanol was allowed to stand at room temperature for 5 weeks. It was then deacidified with 10 g of solid sodium bicarbonate (overnight), filtered, and concentrated; the residual liquid was distilled to give 3.0 g of a colorless liquid, b.p. $45^\circ\text{C}/0.3\text{ mm}$, n_D^{24} 1.4110. The compound was found to be identical (infrared spectrum and physical properties) with ethyl 2-difluoraminoethylcarbamate.*

e. Methyl N-Fluoro-N-(2,2-dinitro-2-fluoroethyl)carbamate

A solution (mainly suspension) of 2.8 g of methyl 2,2-dinitro-2-fluoroethylcarbamate in 350 ml of water was fluorinated at $0-5^\circ\text{C}$ until

* Ibid., p. 24.

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1.0 liter of fluorine was passed into the reaction mixture. The solution was extracted with three 80-ml portions of methylene chloride; the combined extracts were dried, filtered, and concentrated. The residual liquid was distilled to give 1.0 g of a colorless liquid, b.p. 59-61°C/0.1 mm, n_D^{24} 1.4285, that was identified as $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{NFCO}_2\text{CH}_3$. From the distillation residue 1.0 g of starting material was recovered.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{N}_3\text{F}_2\text{O}_6$: C, 20.97; H, 2.20; N, 18.34; F, 16.59
Found: C, 21.2; H, 2.3; N, 18.0; F, 16.8.

The infrared spectrum of the compound is shown in Figure 13.

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained using a CCl_4 solution with TMS and CFCl_3 as internal references. The proton NMR spectrum (Figure 14) consists of an intense singlet at 3.94 ppm assigned to the ester methyl group, $-\text{CO}_2\text{CH}_3$. The doublet of doublets at 5.05 ppm is assigned to the methylene group, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{NF}$ -. The form of the signal is the result of coupling to the $-\text{NF}$ - fluorine ($J = 30.0$ cps) and the $\text{FC}(\text{NO}_2)_2$ - fluorine ($J = 15.5$ cps). The relatively weak signal at 3.68 ppm is unassignable on the basis of the suggested structure and is presumably an impurity.

The fluorine NMR spectrum (Figure 15) consists of a triplet (splitting 30.2 cps) of doublets (splitting 10.2 cps) at +58.14 ppm, assigned to the $-\text{NF}$ - fluorine. The signal is split into a triplet by coupling to the methylene protons, $-\text{CH}_2\text{NF}$ -, and again into doublets by coupling to the $\text{FC}(\text{NO}_2)_2$ - fluorine. The origin of the doublet splitting was confirmed by a decoupling experiment involving the signal at +108.5 ppm that is assigned to the $\text{FC}(\text{NO}_2)_2$ - fluorine. The weak, broadened signal at +109.7 ppm is unassignable on the basis of the structure and is apparently due to an impurity. The proton and fluorine spectra are otherwise entirely consistent with each other and with the structure, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{NFCO}_2\text{CH}_3$.

C. FLUOROAMMONIUM SALTS (A. Remanick)

1. Discussion

Several attempts have been made to prepare fluoroammonium perchlorate by removing dioxane from the 1-to-1 fluoroammonium perchlorate-dioxane

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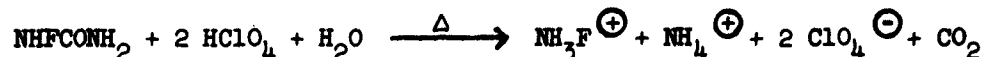
II Technical Discussion, C (cont.)

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complex* at reduced pressure. This procedure has been only partially successful. Thus, the dioxane content of the material was reduced to 4% by subjecting the complex to a pressure of 20 microns (μ) of Hg for 80 hours at room temperature. After an additional 60 hours under these conditions, carbon analysis showed no further loss of dioxane, although the analytical values for fluorine and nitrogen approached the theoretical values for fluoroammonium perchlorate. In another attempt to remove the last traces of dioxane, the temperature was increased to 40-45°C after the bulk of the dioxane was removed at room temperature. At 42-46°C and 20 μ , the residual material sublimed readily, coating the cooler portions of the apparatus with a white solid. Although the sublimate still contained 5.0% dioxane, the results suggested that fluoroammonium perchlorate itself could be sublimed. Work with the dioxane complex was halted at this point, and the purification of crude fluoroammonium perchlorate was resumed.

Crude fluoroammonium perchlorate solution, prepared by hydrolyzing isopropyl N-fluorocarbamate in 70% perchloric acid,** was concentrated under vacuum at room temperature. The resulting semisolid residue was sublimed at 45°C and 20 μ . A white crystalline solid collected on the walls of the apparatus just above the heated zone; it was identified as pure fluoroammonium perchlorate by means of elemental analysis. The pure material is extremely hygroscopic, necessitating the use of an explosion-proof dry box for the experimental work. Efforts to refine the sublimation technique are now underway so that the gram quantities of fluoroammonium perchlorate needed for complete characterization of physical properties can be purified easily and safely.

Fluorourea became available recently, and several attempts were made to use it as an alternate starting material in the synthesis of fluoroammonium perchlorate. Hydrolysis with 70% perchloric acid was expected to proceed as follows:



* Aerojet-General Report 0235-01-18, p. 18.

** Aerojet-General Report 2730, p. 44.

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Carbon dioxide was evolved during the initial stages of the reaction, and the hydrolysis appeared to be proceeding smoothly. Rapid, uncontrolled reaction led to a "fume-off" after approximately one-third the theoretical amount of gas had been collected. A repetition of the reaction, using a more dilute solution of fluorourea in 70% perchloric acid, again terminated with a fume-off. By reducing the reaction temperature to 35°C, control was finally maintained while approximately two-thirds of the theoretical amount of gas was collected. Fluoroammonium perchlorate was not formed. The presence of nitrous oxide in the evolved gas suggests that decomposition of fluorourea occurred.

2. Experimental

a. Removal of Dioxane from Fluoroammonium Perchlorate-Dioxane Complex

Fluoroammonium perchlorate-dioxane complex* (about 100 mg) was placed in a sublimation apparatus and subjected to a pressure of 20 μ at 20-25°C. Analytical samples of the residual solid were removed after periods of 80 and 140 hours.

Anal. Calcd. for $\text{FNH}_3\text{ClO}_4 \cdot \text{C}_4\text{H}_8\text{O}_2$: C, 21.5; H, 4.90; N, 6.6; F, 8.55.

Calcd. for FNH_3ClO_4 : C, 0.0; H, 2.22; N, 10.4; F, 14.0; ClO_4^- , 73.5.

Found (after 80 hours): C, 0.82; H, 2.46; F, 13.1.

Found (after 140 hours): C, 0.80; H, 3.16; N, 10.0; F, 13.9; ClO_4^- , 74.8.

When 1.5 g of the complex was subjected to the same treatment for 140 hours, the residual solid retained 7.8% carbon. A small portion of this solid was placed in a tube and heated to 42-46°C at 20 μ for 3 hours. The contents of the tube sublimed completely, and a white solid collected on the unheated portion of the tube. The sublimate was analyzed, with the following results: C, 1.35; H, 3.86; F, 11.7.

b. Fluoroammonium Perchlorate

Isopropyl N-fluorocarbamate (0.5 g) was hydrolyzed with 2.5 ml of 70% perchloric acid as previously described.** The excess perchloric

* Aerojet-General Report 0235-01-18, p. 18.

** Aerojet-General Report 2730, p. 44.

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acid was removed under vacuum ($20\ \mu$) at room temperature until the residual solution became cloudy. Some of this solution (a few drops) was placed in a tube and heated under vacuum ($46^\circ\text{C}/20\ \mu$) for 24 hours. The major portion of the material sublimed and deposited on the unheated portion of the tube in the form of a white crystalline solid.

Anal. Calcd. for FNH_3ClO_4 : N, 10.4; F, 14.0.

Found: N, 10.3; F, 13.8.

The physical appearance and fluorine content of the material did not change during 24-hour storage in a dry box at room temperature.

c. Reaction of Fluorourea with 70% Perchloric Acid

Three milliliters (about 0.0335 mole) of 70% perchloric acid was added to 0.5 g (0.0064 mole) of fluorourea contained in a round-bottomed flask. The flask was connected to a gas burette and the reaction mixture was heated gradually (1 hour) to 40°C . Gas evolved slowly during this time. The reaction mixture fumed off after 40 min at 40°C . The volume of gas evolved up to that time amounted to 30% of the theoretical amount of carbon dioxide expected.

Repetition of this reaction using 0.78 g (0.010 mole) of fluorourea and 10.0 ml (about 0.115 mole) of 70% perchloric acid again resulted in a fume-off after 21% of the theoretical amount of gas evolved. The gas liberated prior to the fume-off was pure carbon dioxide (based on its infrared spectrum).

A fume-off in the fluorourea-perchloric acid reaction was avoided by lowering the reaction temperature. A solution of 0.5 g (0.0064 mole) of fluorourea in 4.0 ml (about 0.046 mole) of 70% perchloric acid was heated to 35°C in 32 min and was maintained at that temperature for 35 min. During this time, 94 ml of gas was liberated. The last 30 ml of gas liberated was found to be a 70/30% mixture of carbon dioxide and nitrous oxide (based on its infrared spectrum).

The cloudy perchloric acid solution of the reaction products was filtered, and the filtrate was concentrated at $20\text{-}25^\circ\text{C}/20\ \mu$ to give

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a small amount of a white solid that was not the expected fluoroammonium perchlorate. This white solid was not completely identified; it was treated with 0.3 ml of tetrahydrofuran (to dissolve fluoroammonium perchlorate), the solution was filtered, and the filtrate was added to 0.6 ml of dioxane. Fluoroammonium perchlorate-dioxane complex did not precipitate; a trace of solid material, m.p. $> 180^{\circ}\text{C}$, was the only product formed.

III. PERSONNEL

The experimental synthesis work was performed by K. Baum, J. M. Cavallo, F. J. Gerhart, V. Grakauskas, M. P. Mascari, and A. H. Remanick. Analytical support was provided by C. L. Deuel (gas chromatography), K. Inouye (micro-analysis), D. I. Matson (infrared analysis), and H. M. Nelson (NMR).

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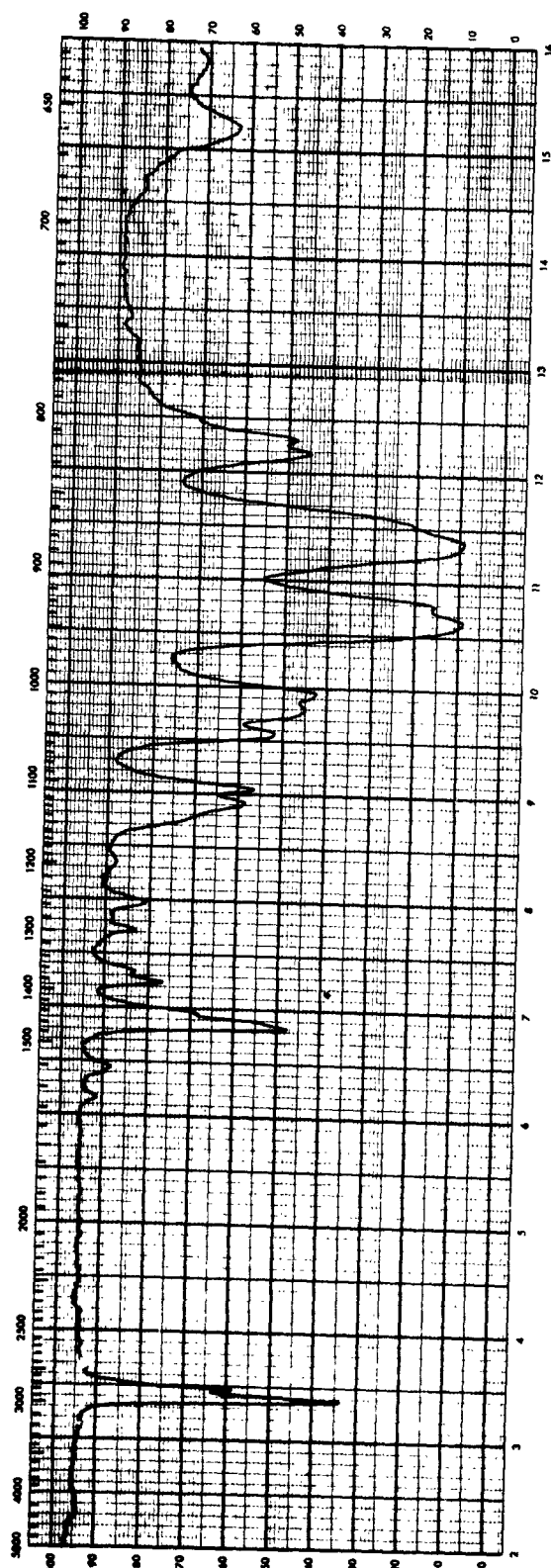


Fig. 1 Infrared Spectrum of 1-Bromo-1,1-bis(difluoramino)butane

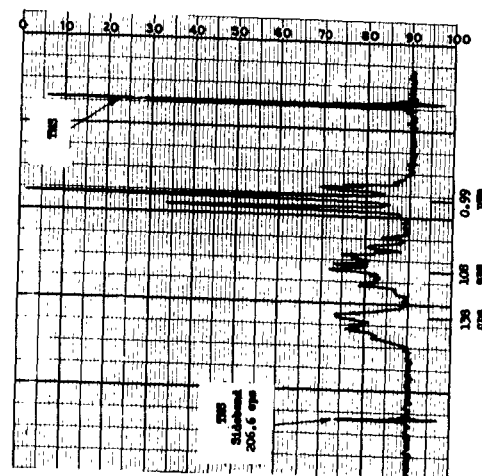


Fig. 2 Proton NMR Spectrum of 1-Bromo-1,1-bis(difluoramino)butane

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Figures 1 and 2

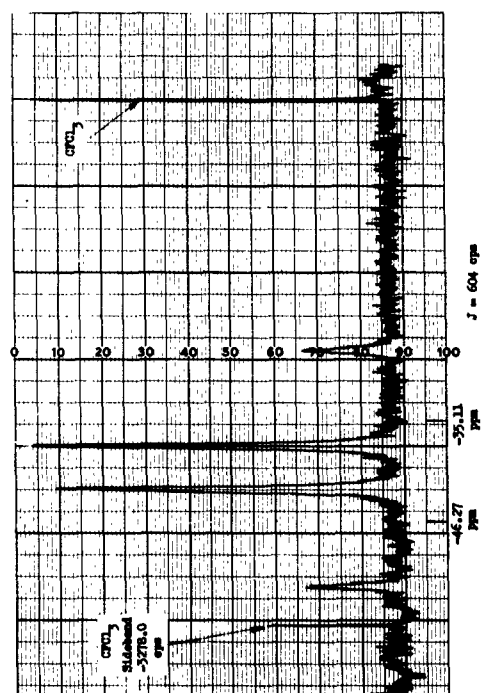


Fig. 3 Fluorine NMR Spectrum of 1-Bromo-1,1-bis(difluoramino)butane

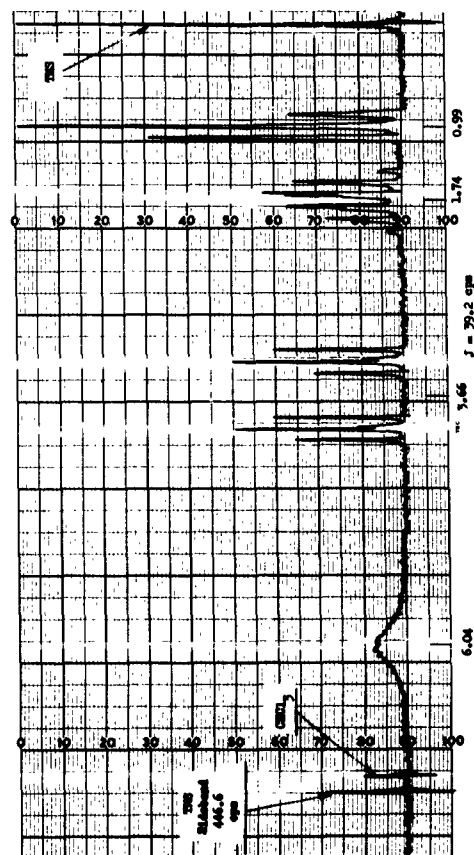


Fig. 4 Proton NMR Spectrum of N-Fluoro-N-n-propylurea

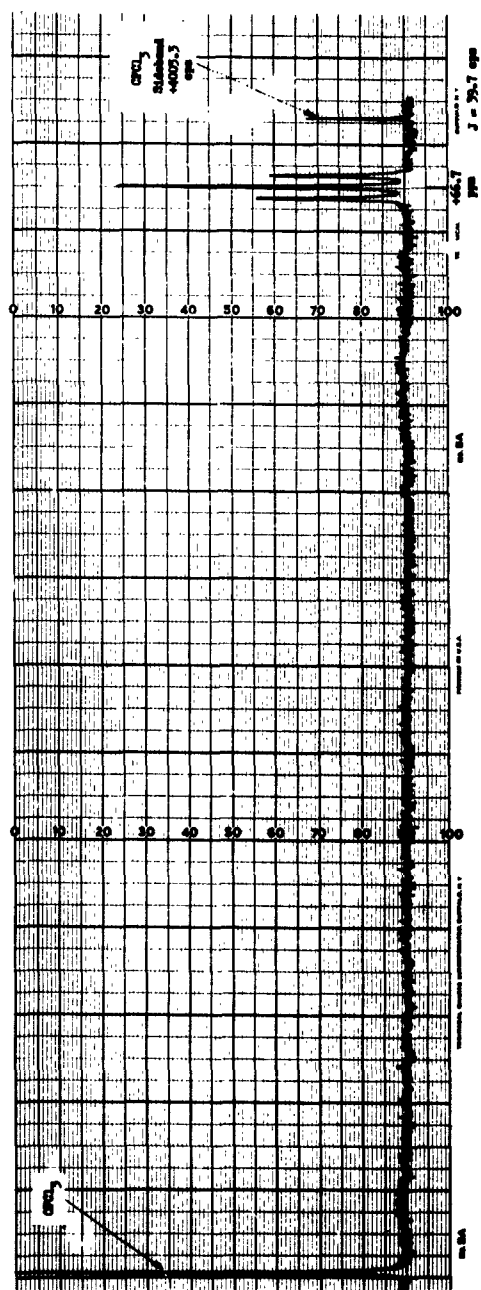


Fig. 5 Fluorine NMR Spectrum of N-Fluoro-N-n-propylurea

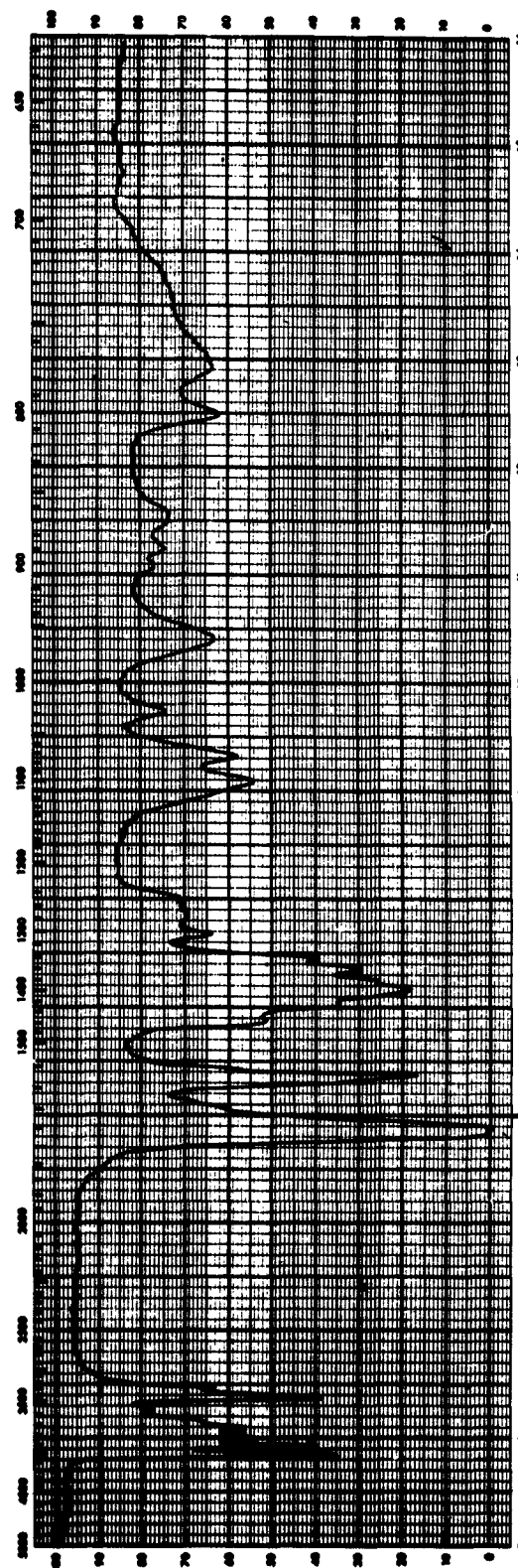


Fig. 6 Infrared Spectrum of N-Fluoro-N-n-propylurea

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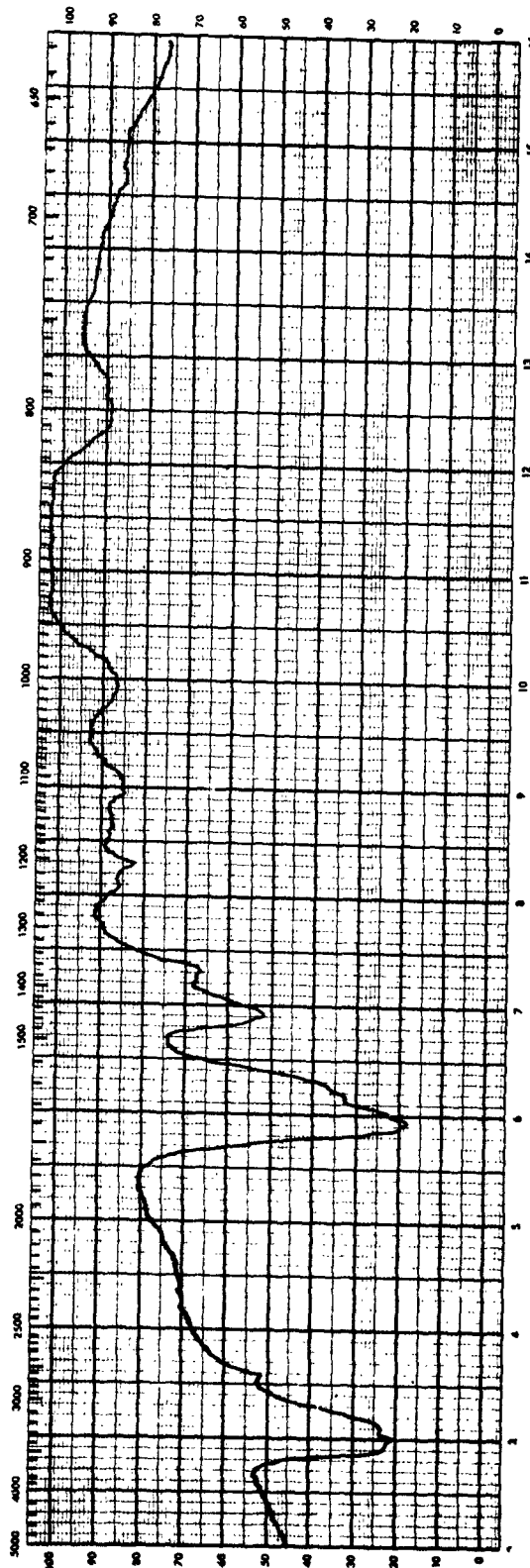


Fig. 7 Infrared Spectrum of Fluorourea

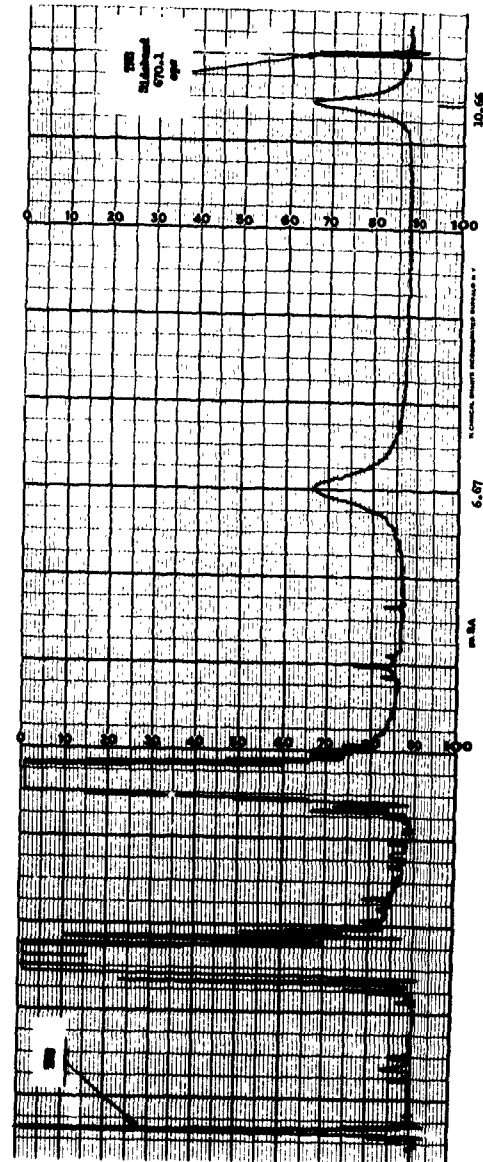


Fig. 8 Proton NMR Spectrum of Fluorourea

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Figures 7 and 8

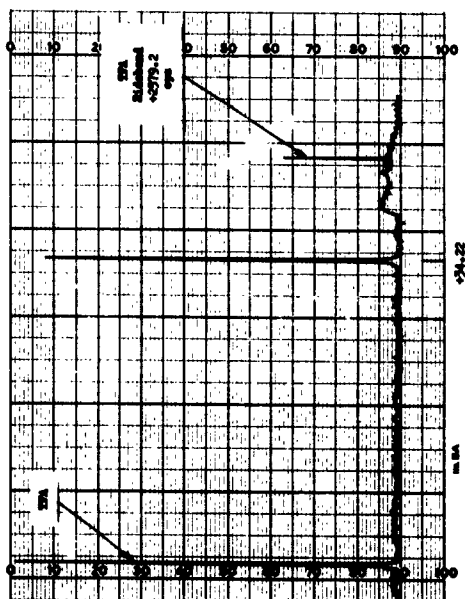


Fig. 9 Fluorine NMR Spectrum of Fluorourea

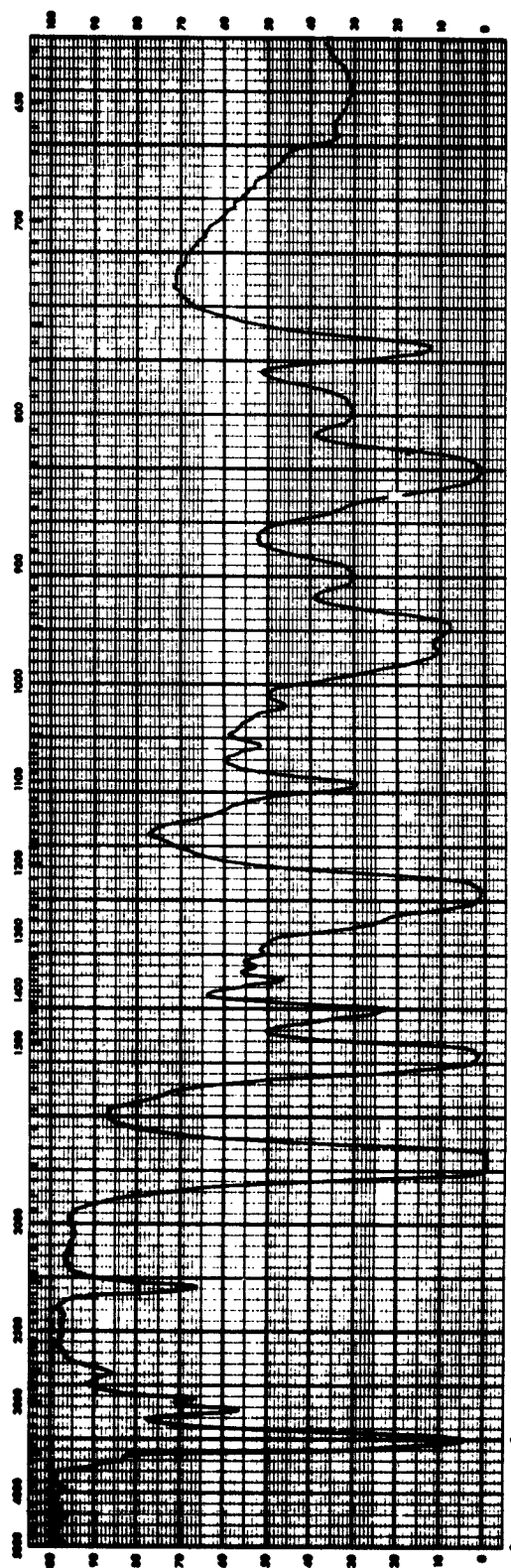


Fig. 10 Infrared Spectrum of 2-Difluorethylcarbonyl Fluoride

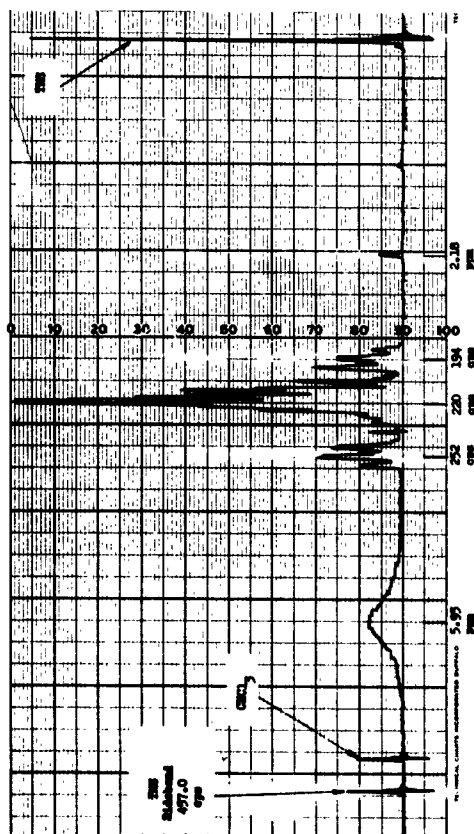


Fig. 11 Proton NMR Spectrum of 2-Difluoraminoethylcarbaryl Fluoride

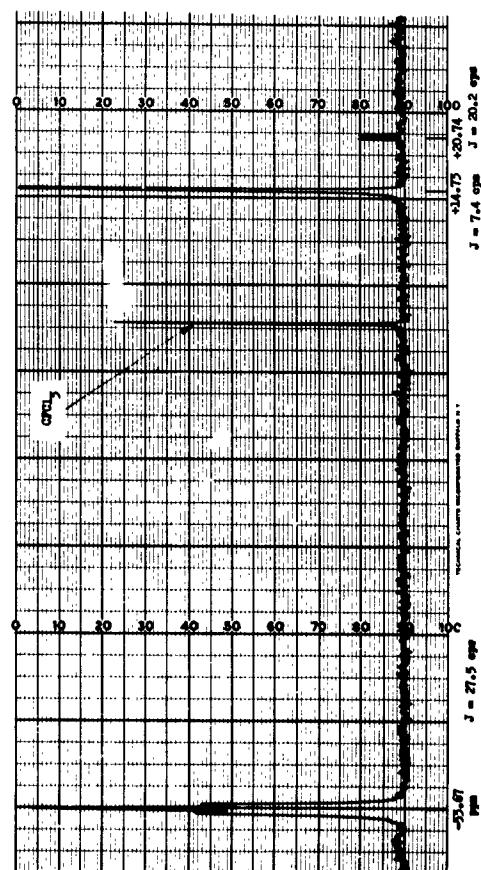


Fig. 12 Fluorine NMR Spectrum of 2-Difluoraminoethylcarbaryl Fluoride

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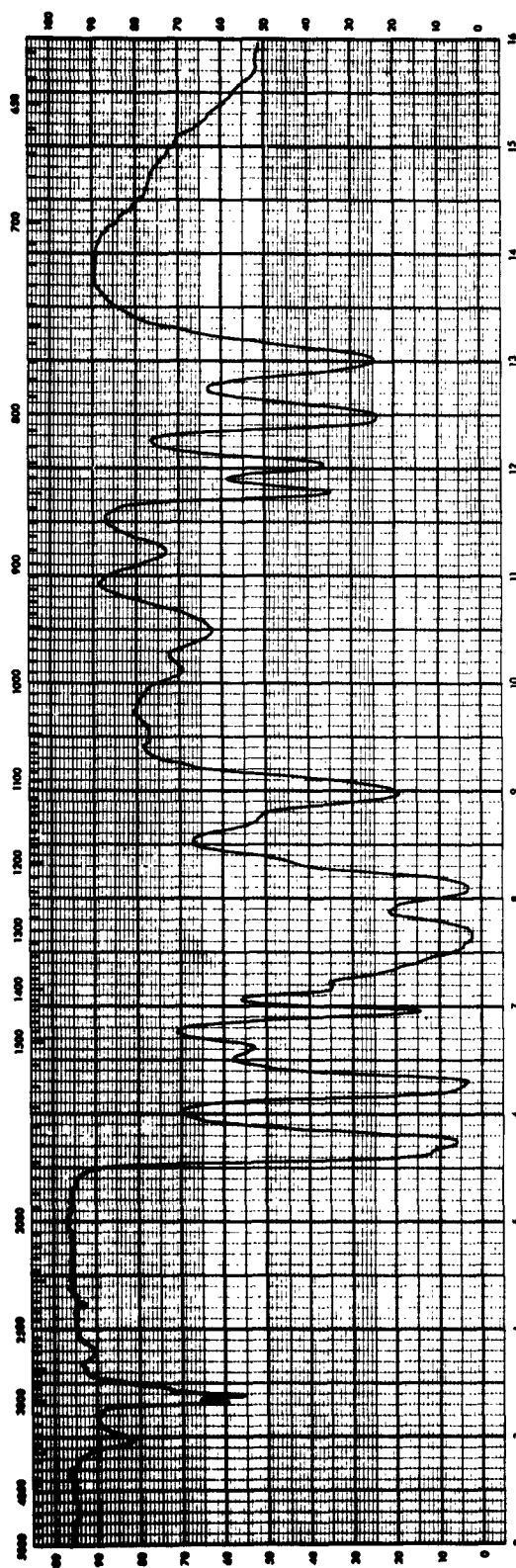


Fig. 13 Infrared Spectrum of Methyl N-Fluoro-N-(2,2-dinitro-2-fluoroethyl)carbamate

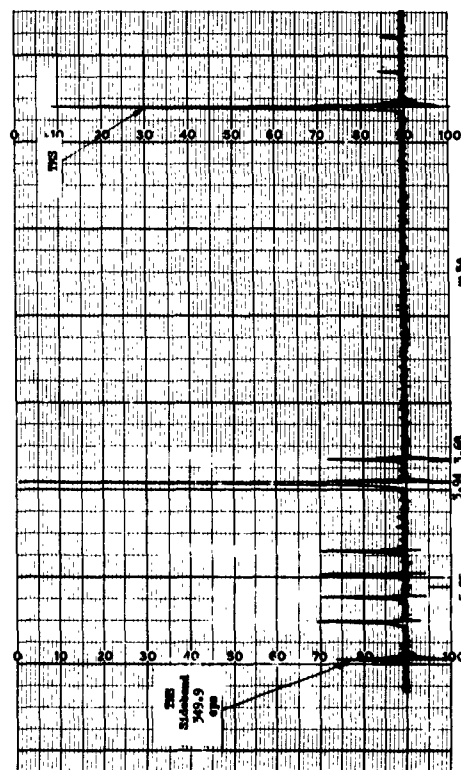


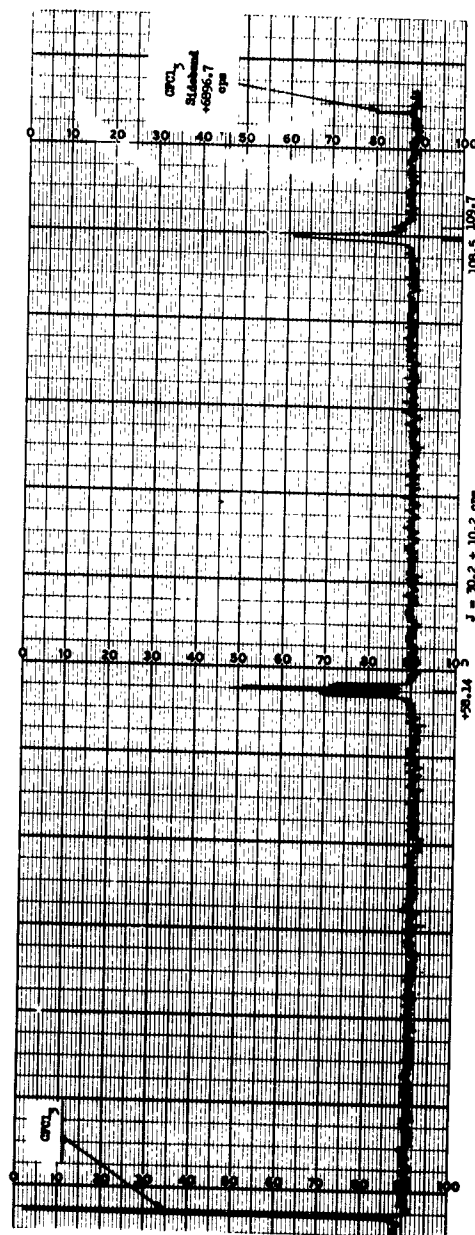
Fig. 14 Proton NMR Spectrum of Methyl N-Fluoro-N-(2,2-dinitro-2-fluoroethyl)carbamate

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Figures 13 and 14

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Fluorine NMR Spectrum of Methyl N-Fluoro-N-(2,2-dinitro-2-fluoroethyl)carbamate

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Figure 15

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